The Laws of Series Spectra.

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Several theories of the production of series spectra have been given in recent years, and it has become apparent that no further real progress can be made in the interpretation of spectra until the true form of the series relations is known more accurately. Various formulæ, such as those of Ritz and Hicks, fit the measured wave-lengths almost equally well, and all demonstrate at least the approximate truth of two fundamental results: (1) that the Diffuse and Sharp series tend to the same limits, and (2) that the difference between the limiting wave-numbers of the Sharp and Principal series is the wave-number of the first Principal line. The first is now usually taken as proved, but no formula has yet made it evident that the second—the Rydberg-Schuster law—is more than a close approximation. One of the objects of this paper is to show that it is an absolute law. Another fundamental question, on which different opinions are held, is that of Rydberg's constant. Hicks* has concluded that this constant may be slightly different in the various series produced by helium. According to Bohr's theory of spectra† it should be an absolute constant for all the ordinary helium series, but different from the hydrogen constant by a calculable amount. The results of this paper tend to show that the constant for arc spectra is absolute, and has the value 109679·22, recently determined by Curtis‡ for hydrogen only, on the International scale of wave-lengths.

The formula for any series, whether Diffuse, Sharp or Principal, is

$$\nu_m = \mathrm{A} - \mathrm{N}/\mathrm{D}_m^2, \tag{1}$$

where ν is the wave number of a line, N is Rydberg's constant, and D_m is a function of an integer m. According to the Hicks formula,

$$\mathrm{D}_m = m + \mu + \alpha/m, \tag{2}$$

where μ and α are constants. The Ritz formula usually quoted makes

$$\mathrm{D}_m = m + \mu + \alpha/m^2, \tag{3}$$

and it has been decided that (3) is not so good as (2), although α is usually

* 'Phil. Trans.,' A, vol. 210, p. 111, 1.
† Phil. Mag.,' vol. 26, pp. 1 and 476 (1913).
‡ 'Roy. Soc. Proc.,' vol. 90, p. 605 (1914).

so small that their difference is not very appreciable. This inferiority nevertheless exists. But the formula on which Ritz* really relied was of the form

$$\nu_m = \mathrm{A} - \mathrm{N}/\{m+\mu+\alpha(\mathrm{A}-\nu)\}^2, \tag{4}$$

not expressing ν explicitly as a function of m, so that the failure of (3), which is only an approximation, is not a conclusive test of Ritz' formula.

This paper will indicate that (4), although unsatisfactory, is probably the best form for this number of constants, without implying, however, that Ritz' theoretical foundation for the formula is correct. Into the question of the origin of series we shall not enter.

Hicks† has made the interesting suggestion that

$$\mathrm{D}_m = m+\mu+\alpha/(m+\mu)+\alpha/(m+\mu)+\ldots, \tag{5}$$

an infinite continued fraction, whose value is

$$\mathrm{D}_m = \tfrac{1}{2}(m+\mu)+\sqrt{[\{\tfrac{1}{2}(m+\mu)\}^2+\alpha]}. \tag{6}$$

The relation between (5) and (2) is very similar to that between Ritz' formula (4) and its approximation.

The conclusions reached in the paper are the result of a consideration of several different spectra which are known with sufficient experimental accuracy to enable a discrimination between the formulæ to be made. In the paper, however, only the spectrum of helium will be dealt with, for it is peculiarly suitable on account of the general accuracy of its abundant series, and the especial accuracy of the first lines of the series, measured by Lord Rayleigh‡ and by Eversheim.§ Moreover, theories of atomic structure are becoming definite in the case of helium, and can only be tested by a more intimate knowledge of the nature of its spectrum. Perhaps at this point we may emphasize the urgent need, to the theoretical spectroscopist, of interferometer measurements of four or five successive lines in any helium series.

The very complete study of the helium spectrum made by Hicks|| does not include the measurements of Eversheim, which are according to the International scale of wave-lengths. This scale must be used in any accurate discussion of spectral formulæ. At the same time, wave-lengths reduced to vacuo must be employed. The reductions to vacuo may be effected by the tables published by Kayser,¶ and they have been applied to all the wave-lengths studied below.

The main novelty in the treatment consists of a method for the accurate

* 'Ann. der Phys.,' vol. 25, p. 660 (1908).

† 'Phil. Trans.,' A, vol. 210, p. 60 (1910).

‡ 'Phil. Mag.' (6), vol. 15, p. 548 (1908).

§ 'Kayser's Handbuch,' vol. 5, p. 520.

|| *Loc. cit.*

¶ 'Handbuch der Spectroscopie,' vol. 2, p. 576.

determination of the limits of series, which requires, for its application, a preliminary formula, for example of the Hicks type, for the expression of the series.

The Diffuse or First Subordinate Series of Helium.

Hicks has represented this series with great accuracy by the formula

$$\nu = 29222{\cdot}595 - 109689{\cdot}2/\{m + 0{\cdot}996347 + 0{\cdot}002200/m\}^2. \qquad (7)$$

The lines are doublets, and the formula relates to their more refrangible components.

In the following Table are the wave-lengths (λ) and wave numbers (ν) of the lines of this series. The first two are Eversheim's, and the others are Runge and Paschen's, reduced to the International scale by the corrections published recently by Kayser.* All have been reduced to vacuo.

m.	λ in Å.	$\nu = 10^8\lambda^{-1}$.	m.	λ in Å.	$\nu = 10^8\lambda^{-1}$.
2	5877·240	17014·789	9	3555·440	28125·912
3	4472·724	22357·740	10	3531·486	28316·689
4	4027·308	24830·479	11	3513·485	28461·766
5	3820·664	26173·459	12	3499·614	28574·581
6	3706·034	26983·021	13	3488·704	28663·941
7	3635·258	27508·362	14	3479·934	28736·170
8	3588·280	27868·503	15	3472·764	28795·506

The last figures in λ are not all exact, and, in certain cases, the errors, which are larger than were estimated by Runge and Paschen, amount to 1/100 of an Ångstrom unit. In the following investigation, however, where the limit is calculated from every pair of successive lines, the mean must be very accurate if the errors in the lines are not systematic.

The Hicks formula shows that they can be represented by

$$\nu_m = \mathrm{A} - \mathrm{N}/(m + \delta + 1)^2, \qquad (8)$$

where δ never exceeds 0·004. If this be expanded

$$\nu_m = \mathrm{A} - \frac{\mathrm{N}}{(m+1)^2}\left[1 - \frac{2\delta}{m+1} + \frac{3\delta}{(m+1)^2}\cdots\right].$$

The fourth term of this very convergent series is $3\mathrm{N}\delta^2/(m+1)^4$. Since N is about 10^5, this cannot exceed

$$3 \,.\, 10^5 \,.\, 16 \,.\, 10^{-6} \,.\, 3^{-4} = 0{\cdot}06,$$

even when $m = 2$. If we take all the lines beyond $m = 3$, it cannot exceed 0·007, so that for all these lines

$$\nu_m = \mathrm{A} - \mathrm{N}/(m+1)^2 + 2\mathrm{N}\delta/(m+1)^3;$$

* 'Handbuch der Spectroscopie,' vol. 6, p. 891.

or
$$
\begin{aligned}
(m+1)^3 \nu_m &= A(m+1)^3 - N(m+1) + 2N\delta, \\
(m+2)^3 \nu_{m+1} &= A(m+2)^3 - N(m+2) + 2N\delta, \\
(m+3)^3 \nu_{m+2} &= A(m+3)^3 - N(m+3) + 2N\delta.
\end{aligned}
$$
and
$$A = \frac{(m+2)^2 \nu_{m+1} - (m+1)^2 \nu_m + N}{(m+2)^3 - (m+1)^3}. \tag{9}$$

If the value of N were known, this formula would permit a determination of the limit of the series from any pair of consecutive lines. Actually, the exact value of N is one of the objects of the investigation, but we know that it cannot differ greatly, whether on a definite theory such as Bohr's, or on the results of the calculations of Hicks, from Curtis' value for hydrogen. We may therefore write $N = 109679{\cdot}22 + \delta N$, where δN represents the divergence of the value from that of Curtis, and treat δN as a small unknown magnitude. The calculated limit for any two lines is then of the form $C + B\delta N$, where C and B are numerical, and B is a very small coefficient, of order, as appears later, about 10^{-4}. A series of values of this type are then obtained, and their mean, taken in accord with the usual methods, must be much more accurate than the value of the limit calculated, by the ordinary methods, by fitting an empirical formula to the leading lines of the series. For, in the present method, every line, beyond say $m = 3$, will be used twice.

This final mean limit involves δN as an unknown quantity, and, in fact, the basis of the method consists of converting the ordinary uncertainty regarding the limit into a definite function of the uncertainty in the value of N. In this way it becomes possible to proceed, without a more definite determination of the limit, just as though that limit were accurately found, for the degree of uncertainty is known as an exact function of δN.

One or two remarks may be made at this point. Although a Hicks formula is our starting point, the small systematic deviations given by any Hicks formula for the higher lines do not enter into the calculated sequence of limits, whose mean is finally taken. They would be detected, if present, by a systematic change in the calculated limits, and, as pointed out later, when these are calculated this effect does not occur. On the other hand, from the mathematical point of view, the binomial development used above does not admit of their occurrence, being remarkably independent, in its final results, of small changes in the value of $m+\mu$ adopted.

The small differences between our limits and those of Hicks are not entirely due to the use of International units.

The Sharp or Second Subordinate Series of Helium.

The Hicks formula for this series is

$$\nu_m = 29222{\cdot}696 - 109719{\cdot}6/\{m + 0{\cdot}705092 - 0{\cdot}013408/m\}^2, \tag{10}$$

and the lines, corrected to the International scale and for the refractive index of air, are shown in the next Table. The first two are Eversheim's absolute measurements.

m.	λ.	ν.	m.	λ.	ν.
2	7067·123	14150·028	9	3563·973	28058·572
3	4714·448	21211·389	10	3537·804	28266·120
4	4121·963	24260·284	11	3518·316	28422·686
5	3868·537	25849·564	12	3503·302	28544·496
6	3733·894	26781·690	13	3491·602	28640·146
7	3652·991	27374·826	14	3482·432	28715·562
8	3600·329	27775·237			

The Hicks formula is of the type

$$\nu_m = \mathrm{A} - \mathrm{N}/(m + 0{\cdot}7 + \delta)^2, \tag{11}$$

where, after $m = 3$, δ never exceeds 0·004, so that the preceding method can be applied, giving

$$\mathrm{A} = \frac{(m+1{\cdot}7)^3\,\nu_{m+1} - (m+0{\cdot}7)^3\,\nu_m + \mathrm{N}}{(m+1{\cdot}7)^3 - (m+0{\cdot}7)^3}. \tag{12}$$

The Principal Series.

In this case the Hicks formula is

$$\nu = 38453{\cdot}347 - 109666{\cdot}2/\{m + 0{\cdot}929442 + 0{\cdot}007792/m\}^2. \tag{13}$$

Only the first line has been measured by an interference method. The probable correction required to reduce it to vacuo has been found by interpolation from Kayser's Tables as 2·53 Å.U. Paschen gives its wave-length as 10830·30 Å.U., measured by the interferometer.*

m.	λ.	ν.	m.	λ.	ν.
1	10832·83	9231·198	6	2764·600	36171·595
2	3889·715	25708·822	7	2723·965	36711·188
3	3188·603	31361·695	8	2696·914	37079·413
4	2945·954	33944·858	9	2677·880	37342·967
5	2829·879	35337·197	10	2663·976	37537·869

* Trans. Intern. Union Solar Research, Bonn, 1913.

Beyond $m = 2$ even, we may take the denominator in Hicks' formula as $(m+0\cdot930+\delta)^2$, where δ is of order $0\cdot002$ at most. Then, for $m = 3$,

$$3\mathrm{N}\delta^2/(m+0\cdot93)^4 = 0\cdot005,$$

and is negligible. Thus we may write, beyond $m = 2$,

$$\mathrm{A} = \frac{(m+2\cdot93)^3\,\nu_{m+2}-(m+1\cdot93)^3\,\nu_{m+1}+\mathrm{N}}{(m+2\cdot93)^3-(m+1\cdot93)^3}. \tag{14}$$

The next section exhibits the results of these calculations.

Limits of the Series.

For the Diffuse series, using lines beyond $m = 3$, successive values of the limits are

$$\left.\begin{array}{ll} \mathrm{A} = 29223\cdot478+\delta\mathrm{N}/91, & \mathrm{A} = 29223\cdot530+\delta\mathrm{N}/127, \\ \quad\;\; 29223\cdot577+\delta\mathrm{N}/169, & \quad\;\; 29223\cdot671+\delta\mathrm{N}/217, \\ \quad\;\; 29223\cdot072+\delta\mathrm{N}/271, & \quad\;\; 29224\cdot412+\delta\mathrm{N}/331, \\ \quad\;\; 29224\cdot429+\delta\mathrm{N}/397, & \quad\;\; 29224\cdot085+\delta\mathrm{N}/469, \\ \quad\;\; 29223\cdot354+\delta\mathrm{N}/547, & \quad\;\; 29224\cdot149+\delta\mathrm{N}/631. \end{array}\right\} \tag{15}$$

No value of $\delta\mathrm{N}$ can be found which makes the general deviations from equality any smaller than they are for the calculated parts at present—a first indication that $\delta\mathrm{N} = 0$.

If $\delta\mathrm{N}$ exists the other portions should become progressively larger, and this does not occur either here, or with the Sharp and Principal series.

The mean value is

$$\mathrm{A} = 29223\cdot776+0\cdot004416\,\delta\mathrm{N}, \tag{16}$$

and differs only slightly from each individual value. As there are 10 of these we may attach considerable accuracy to the mean. $\delta\mathrm{N}$ denotes the increase of the value of N beyond that of Curtis. It is noteworthy that the value chosen for N makes only a minute difference in the limit, if the variations of N are of the order hitherto suggested.

The application of the same process to the Sharp series gives the values

$$\left.\begin{array}{ll} \mathrm{A}' = 29225\cdot350+0\cdot01229\,\delta\mathrm{N}', & 29224\cdot386+0\cdot00865\,\delta\mathrm{N}', \\ \quad\;\;\; 29224\cdot170+0\cdot00642\,\delta\mathrm{N}', & 29223\cdot373+0\cdot00495\,\delta\mathrm{N}', \\ \quad\;\;\; 29224\cdot154+0\cdot00393\,\delta\mathrm{N}', & 29223\cdot648+0\cdot00320\,\delta\mathrm{N}', \\ \quad\;\;\; 29223\cdot279+0\cdot00265\,\delta\mathrm{N}', & 29226\cdot665+0\cdot00224\,\delta\mathrm{N}', \\ \quad\;\;\; 29224\cdot514+0\cdot00191\,\delta\mathrm{N}', & 29217\cdot241+0\cdot00165\,\delta\mathrm{N}'. \end{array}\right\} \tag{17}$$

The general mean is

$$\mathrm{A}' = 29223\cdot678+0\cdot00479\,\delta\mathrm{N}', \tag{18}$$

but a more accurate value will be obtained by attaching weights of $\frac{1}{2}$ to the first, eighth and tenth values, which differ considerably from the others.

We notice that in the 10 values of A′ or of A, there is not a systematic increase or decrease, whether δN, $\delta N'$ are zero or not. This illustrates the remark on an earlier page that the method does not involve the systematic small deviations usually given by a Hicks formula for the higher lines (in order of m) in any series.

The resulting weighted mean is

$$A' = 22223{\cdot}780 + 0{\cdot}00468\,\delta N'. \tag{19}$$

More exhaustive treatment does not appreciably alter this value.

The Principal series, treated in the same way beyond $m = 3$, gives the values

$$\left.\begin{array}{lll} A'' = 38451{\cdot}831 + 0{\cdot}0169\,\delta N'', & & 38454{\cdot}435 + 0{\cdot}0113\,\delta N'', \\ 38454{\cdot}052 + 0{\cdot}0080\,\delta N'', & & 38455{\cdot}155 + 0{\cdot}0060\,\delta N'', \\ 38453{\cdot}563 + 0{\cdot}0047\,\delta N'', & & 38456{\cdot}579 + 0{\cdot}0038\,\delta N'', \\ 38457{\cdot}993 + 0{\cdot}0031\,\delta N'', & & \end{array}\right\} \tag{20}$$

The general mean is

$$A'' = 38454{\cdot}801 + 0{\cdot}00768\,\delta N'', \tag{21}$$

from which we see that if $\delta N''$ is not large, the only bad values are the first and last. Now the first pertains to the lines most readily measured, and we must conclude that the strict applicability of the method has not commenced at this stage, so that the first two lines at least should be weighted on this account. A similar error of opposite sign does not appear in the second value, as it should if an error of measurement accounted for the discrepancy in the first value, according to the method used for the calculation. The divergencies in the first and last values practically balance, so that the general mean must be nearly accurate, so far as casual observational errors are concerned. By attaching weights 1, 2, 3, 4, 5, 6 to the first six values, corresponding roughly to the degree to which the formula is applicable, and a weight 1 to the last value, we shall obtain a mean nearly free from errors in formula.

The result is $\qquad A'' = 38454{\cdot}943 + 0{\cdot}00622\,\delta N'', \qquad (22)$

and this result must possess considerable accuracy, beyond, in fact, the accuracy of individual lines.

We may now consider the values of δN, $\delta N'$, $\delta N''$. The limits are

$$\left.\begin{array}{rl} A = & 29223{\cdot}776 + 0{\cdot}004416\,\delta N \text{ (Diffuse)}, \\ A' = & 29223{\cdot}780 + 0{\cdot}00468\ \ \delta N' \text{ (Sharp)}, \\ A'' = & 38454{\cdot}943 + 0{\cdot}00622\ \ \delta N'' \text{ (Principal)}. \end{array}\right\} \tag{23}$$

If Curtis' value is used, or if N is an absolute constant for arc spectra, $\delta N = \delta N' = \delta N''$, and $A = A'$ with extraordinary closeness, so that the Diffuse and Sharp limits are identical. The simple Hicks formulæ make them differ by 0·1. Moreover, the Rydberg-Schuster law gives us the wave number of the first Principal line,

$$\nu = 38454{\cdot}943 - 29223{\cdot}780 = 9231{\cdot}163', \tag{24}$$

against the practical value 9231·198. The agreement is almost exact, and that both these laws should be fulfilled so exactly at the same time is a convincing reason for belief in both, and also in the fact that Curtis' value pertains to helium. Even the minimum value of δN required by Bohr's theory, if the arc spectrum of helium behaved like the spark series discovered by Fowler, is only 44·8, but this makes a serious difference in the limits of the Diffuse and Sharp series. Since, however, no method has been suggested by which the theory can produce the arc spectrum of helium, and such a suggestion appears to be impossible,* we cannot now go into this question. But attention must be called to the extreme sensitiveness of this mode of testing the Rydberg-Schuster law, if many lines in the series are known.

After the proof in later sections that $\delta N = 0$, it is possible to say that the laws of limits are exact. The actual limits deduced are not quite those of Hicks, which give a difference of about 0·4 in the Rydberg-Schuster law. Such a difference can be proved not to arise from the difference between Rowlands' and the International scale, which can only account for a quarter of the effect. The method of the paper, therefore, definitely tends to confirm the Rydberg-Schuster law, which has now been shown to be correct to six significant figures in either limit.

The Series Formula.

The present section is designed to show that three ideas—the Rydberg-Schuster law, Curtis' value of the universal constant, and Rydberg's hypothesis that wave numbers of series lines are functions not of an integer m, but of $m + \mu$, where μ is the 'phase' of the series—are intimately bound together, and that if we assume any one of them, the others follow as necessary consequences of a strict examination of any well-measured spectrum. In the opinion of the writer, this fact is a conclusive proof for the truth of all three. We shall examine, in the most minute manner allowed by the measurements, the Sharp series of helium, with the preliminary remark that the results

* 'Phil. Mag.,' March and July, 1914.

obtained are not peculiar to helium. The idea assumed will be the Rydberg-Schuster law.

The Sharp series has the form

$$\nu_m = \mathrm{A}' - \mathrm{N}'/\rho_m^2,$$

where ρ_m is of an unknown form at present. If $\mathrm{N}' = 109679{\cdot}22 + \delta\mathrm{N}$, the form becomes

$$\nu_m = 29223{\cdot}780 + 0{\cdot}00468\,\delta\mathrm{N}' - (0{\cdot}109679{\cdot}22 + \delta\mathrm{N}')/\rho_m^2, \tag{25}$$

where $\nu_2 = 14150{\cdot}028, \qquad \nu_3 = 21211{\cdot}389, \qquad \nu_4 = 24260{\cdot}284,$

the first two being the extremely accurate measurements of Eversheim.

By the Rydberg-Schuster law, ν_1 is minus the wave number of the first principal line, or

$$\nu_1 = -9231{\cdot}198.$$

The corresponding values of ρ_m can be calculated from (25), and to the first order in $\delta\mathrm{N}$, become

$$\left.\begin{aligned} \rho_1 &= 1{\cdot}688836 + 0{\cdot}0759\,\delta\mathrm{N}, \\ \rho_2 &= 2{\cdot}697438 + 0{\cdot}01187\,\delta\mathrm{N}, \\ \rho_3 &= 3{\cdot}699824 + 0{\cdot}01578\,\delta\mathrm{N}, \\ \rho_4 &= 4{\cdot}700763 + 0{\cdot}01921\,\delta\mathrm{N}. \end{aligned}\right\} \tag{26}$$

Being mainly founded on interference measurements, and on the calculation of close limits from every pair of later lines, these values are more accurate than any previously used in series calculations.

We may test, in turn, the various forms which have been suggested for ρ_m, treating $\delta\mathrm{N}$ as a small unknown quantity. The only suggestions regarding the existence of $\delta\mathrm{N}$ are (1) that it exists (or may exist) as a small positive quantity, not greater than about 130 in helium (Hicks), and (2) that it has the value $+\ 44{\cdot}8$ required by Bohr's theory.

We shall begin with the two-constant formulæ for ρ_m. Hicks has suggested that the form

$$\rho_m = m + \mu + \alpha/m \tag{27}$$

is exact. If this be the case,

$$\begin{aligned} 1 + \mu + \alpha \quad &= 1{\cdot}688836 + 0{\cdot}0^5759\,\delta\mathrm{N}, \\ 2 + \mu + \alpha/2 &= 2{\cdot}697438 + 0\ 0^41187\,\delta\mathrm{N}, \\ 3 + \mu + \alpha/3 &= 3{\cdot}699924 + 0{\cdot}0^41578\,\delta\mathrm{N}, \end{aligned}$$

and the solution of these equations yields

$$\delta\mathrm{N} = 194{\cdot}3, \tag{28}$$

a value too large for either of the suggested changes in N.

It is five times Bohr's value.

The approximate Ritz form is

$$\rho_m = m+\mu+\alpha/m^2,$$

and when treated in the same manner for the first three lines, which are sufficiently accurately measured to determine δN precisely, yields

$$\delta N = -255{\cdot}2, \tag{29}$$

This is both large and negative, and the formula is therefore not so good as that of Hicks. This fact is in agreement with ordinary experience, which shows that the formula is also less satisfactory in other respects.

Hicks has suggested

$$\rho_m = m+\mu+\alpha/(m+\mu)+\alpha/(m+\mu)+\ldots,$$

which is equivalent to

$$\rho_m = \tfrac{1}{2}(m+\mu)+\tfrac{1}{2}\sqrt{\{(m+\mu)^2+4\alpha\}}. \tag{30}$$

The application of this formula is more complicated, and need not be given in detail. It leads to the value

$$\delta N = 776, \tag{31}$$

so that the formula cannot be entertained.

The proper Ritz formula makes

$$\rho_m = m+\mu+\beta(A'-\nu_m) = m+\alpha+\gamma\nu_m \quad \text{(say)}, \tag{32}$$

dependent on the wave number explicitly as well as implicitly.

If this be employed,

$$1+\alpha-9231{\cdot}198\gamma = \rho_1,$$
$$2+\alpha+14150{\cdot}028\gamma = \rho_2,$$
$$3+\alpha+21211{\cdot}389\gamma = \rho_3,$$

where ρ_1, ρ_2, ρ_3, are given by (26). This leads on solution to

$$\delta N = 86{\cdot}7. \tag{33}$$

This value is nearer the accepted limits of possible variation of N, and the formula is therefore better than any of those preceding.

We shall not give the further discussion of the formula, but it is sufficient to say that if this value of δN is used and the other constants calculated, the ensuing wave numbers for the lines corresponding to $m = 4$ and $m = 5$ are not quite satisfactory. They are, however, better than those given by any of the preceding formulæ. Another mode of attack is to calculate the value of δN furnished by the lines $m = 2$, 3, 4, which are measured with sufficient accuracy. It becomes $\delta N = 53{\cdot}1$, differing somewhat from the preceding value, but very close to zero in comparison with the others. A variation of this amount in N has little effect on later lines, and we may conclude that a true

Ritz formula, with N = 109740·0, is remarkably accurate for the Sharp series of helium, but that it does not obey the Rydberg-Schuster law accurately. This utility of the Ritz formula is significant later, for it involves ρ_m as a function of $m + \mu$ rather than of m.

Many other two-constant laws for ρ_m have been examined, but none are satisfactory, the test of a satisfactory law being that δN does not exceed a certain rough value, and that it shall be at least approximately the same whether calculated from $m = 1, 2, 3$, or $m = 2, 3, 4$. The conclusion has been reached that no formula with only two constants in ρ_m can obey the Rydberg-Schuster law, and represent the Sharp series accurately. It is, in fact, a matter of practical experience among spectroscopists that the deviations given by all such laws, however small, are systematic for the lines with the higher values of m. We now see that this is not due to uncertainty about the limit of the series.

One of these remaining laws, however, is of special interest later. If we write

$$\rho_m = m+\mu+\alpha/(m+\mu), \tag{34}$$

we have a two-constant law satisfying Rydberg's opinion that $(m+\mu)$ is the important parameter in ρ_m. This makes

$$(1+\mu)^2+\alpha = (1+\mu)\,\rho_1,$$

$$(2+\mu)^2+\alpha = (2+\mu)\,\rho_2,$$

$$(3+\mu)^2+\alpha = (3+\mu)\,\rho_3,$$

or

$$\mu = \frac{2\rho_2-\rho_1-3}{2+\rho_1-\rho_2} = \frac{3\rho_2-2\rho_3-5}{2+\rho_2-\rho_3}.$$

The value of δN is therefore given by an easy calculation, and becomes $\delta N = 830$.

The formula is therefore not a good one, and when we compare it with that of Ritz, the best yet treated, we reach an interesting conclusion. For the true Ritz formula has for its second approximation

$$\rho_m = m+\mu+\beta/(m+\mu)^2; \tag{35}$$

and if the true form is

$$\rho_m = m+\mu+\alpha/(m+\mu)+\beta/(m+\mu)^2,$$

then α is less important than β. This conclusion is confirmed later.

Three-Constant Formulæ for ρ_m.

If any of the preceding formulæ are first approximations to the truth, their systematic generalisation by the addition of more constants should lead to better results. In this section, we shall treat the Hicks formula, and the

formula last quoted, in this manner, and it will become apparent that a definite conclusion as regards these formulæ can be reached. But this conclusion is actually a general one as regards three- or four-constant formulæ, for many have been tried which we have not space to mention. Throughout the work one formula has stood out with special excellence, and the contingent circumstance that it preserves Rydberg's absolute constant is a further indication of its truth. In view of the especial accuracy of the lines which are used, the success of this formula is more significant than those of formulæ applied to lines of less accuracy in previous investigations.

The first generalisation of the Hicks formula is

$$\rho_m = m+\mu+\alpha/m+\beta/m^2, \tag{36}$$

and if it be applied to the first four lines,

$$\begin{aligned} 1+\mu+\alpha+\beta &= \rho_1, \\ 2^3+2^2\mu+2\alpha+\beta &= 2^2\rho_2, \\ 3^3+3^2\mu+3\alpha+\beta &= 3^2\rho_3, \\ 4^3+4^2\mu+4\alpha+\beta &= 4^2\rho_4. \end{aligned}$$

The elimination of μ, α, β, can be performed at once by a well known theorem of algebra, to the effect that if r and p are integers, and a and b any quantities,

$$\begin{aligned} (a+pb)^r-\frac{p}{1}\{a+(p-1)b\}^r+\frac{p(p-1)}{2!}\{a+(p-2)b\}^r-\ldots &= 0 \quad \text{if } r<p \\ &= b^p r! \text{ if } r=p. \end{aligned} \tag{37}$$

In particular, choosing $a = b = 1$, $p+1 = n$,

$$\begin{aligned} n^r-\frac{n-1}{1!}(n-1)^r+\frac{(n-1)(n-2)}{2!}(n-2)^2-\ldots &= 0 \quad \text{if } r<n-1 \\ &= n-1! \text{ if } r=n-1. \end{aligned} \tag{38}$$

In the present case $n = 4$ and we find

$$4^2\rho_4-3.3^2\rho_3+3.2^2\rho_2-\rho_1 = 6.$$

Substituting the values in (26), we find

$$\delta N = 165{\cdot}8, \tag{39}$$

which is better than the preceding value with the simpler formula, but nevertheless not good. Any formula must be expected to give rather a better value when it contains an extra constant.

If we add yet another constant, and write

$$\rho_m = m+\mu+\alpha/m+\beta/m^2+\gamma/m^3, \tag{40}$$

then δN is determined by

$$5^3\rho_5 - 4 \,.\, 4^3\rho_4 + 6 \,.\, 3^3\rho_3 - 4 \,.\, 2^3\rho_2 + \rho_1 = 4\,! = 24,$$

and substitution of the values in (26) with the addition of $\rho_5 = 5{\cdot}701324 + 0{\cdot}0^4169\,\delta N$, yields $\delta N = 20{\cdot}4$. It is evident, therefore, that with the addition of more constants to the Hicks formula, δN is converging to a small value. The values to be expected are zero or $44{\cdot}8$ (Bohr), but the convergence in the case of the Hicks formula is evidently slow, and the number of constants already contained, which is just sufficient to bring δN into the neighbourhood of the expected values, indicates that the formula is not of the best type. In other words, although ρ_m must be capable of development in the form of a series like (40), in descending powers of m, the development is not convergent enough for the smaller values of m. A development in some other inverse power is required, and Rydberg's theory is at once suggested, according to which

$$\rho_m = m + \mu + \alpha/(m+\mu) + \beta/(m+\mu)^2 + \ldots, \tag{41}$$

where the coefficients α, β, ..., decrease more rapidly than in the Hicks form, is the natural form of ρ_m. We have already tried the case in which only α is retained. It gives $\delta N = 830$. The accompanying value of the phase μ is found to be

$$\mu = 0{\cdot}7282.$$

The comparative success of the true Ritz formula indicates that Rydberg's formula is on the right lines.

Absolute Character of the Rydberg Constant.

We may now retain another constant and write

$$\rho_m = m + \mu + \alpha/(m+\mu) + \beta/(m+\mu)^2,$$

so that

$$\begin{aligned}
(1+\mu)^3 + \alpha\,(1+\mu) + \beta &= (1+\mu)^2\,\rho_1,\\
(2+\mu)^3 + \alpha\,(2+\mu) + \beta &= (2+\mu)^2\,\rho_2,\\
(3+\mu)^3 + \alpha\,(3+\mu) + \beta &= (3+\mu)^2\,\rho_3,\\
(4+\mu)^3 + \alpha\,(4+\mu) + \beta &= (4+\mu)^2\,\rho_4.
\end{aligned}$$

Elimination of α and β from the first three equations gives the quadratic for μ,

$$\mu^2\,\{\rho_3 + \rho_1 - 2\rho_2\} + \mu\,\{6\rho_3 - 8\rho_2 + 2\rho_1 - 6\} + \{9\rho_3 - 8\rho_2 + \rho_1 - 12\} = 0, \tag{42}$$

and from the last three,

$$\mu^2\,\{\rho_4 - 2\rho_3 + \rho_2\} + \mu\,\{8\rho_4 - 12\rho_3 + 4\rho_2 - 6\} + \{16\rho_4 - 18\rho_3 + 4\rho_2 - 18\} = 0. \tag{43}$$

A value of δN must be selected, so that these equations have a root in common.

In the preliminary solution we may neglect the portions of ρ_1, ρ_2, ..., dependent on δN, which are in any case small. The first quadratic then becomes

$$0{\cdot}006216\mu^2+2{\cdot}002888\mu-1{\cdot}407742 = 0,$$

and its solution is $$\mu = 0{\cdot}700133. \tag{44}$$

If the terms in δN are included, μ will be altered by an amount $\delta\mu$, where it is easily shown that

$$\delta\mu\,\{2\mu(\rho_3+\rho_1-2\rho_2)+6\rho_3-8\rho_2+2\rho_1-6\} = -(\mu+1)^2\,\delta\rho_1+2(\mu+2)^2\,\delta\rho_2-(\mu+3)^2\,\delta\rho_3,$$

where $\delta\rho_1 = 0{\cdot}0^5759\,\delta N$, $\delta\rho_2 = 0{\cdot}0^41187\,\delta N$, $\delta\rho_3 = 0{\cdot}0^41578\,\delta N$,

and, finally,

$$\mu = 0{\cdot}700133+0{\cdot}0^43227\,\delta N. \tag{45}$$

The second quadratic is, without terms in δN,

$$0{\cdot}001447\mu^2+2{\cdot}002032\mu-1{\cdot}405128 = 0;$$

and, solving in the same manner,

$$\mu = 0{\cdot}700149+0{\cdot}0^43898\,\delta N. \tag{46}$$

These two values are identical if

$$\delta N = -2{\cdot}38. \tag{47}$$

This is the best result yet obtained, and the improvement made by the addition of one more constant is remarkable. δN is now well within the limits of previously suggested variation of N, and it is almost exactly zero, suggesting that zero is its actual value. Moreover, the calculated value of μ becomes $\mu = 0{\cdot}700056$.

This suggests that μ is converging to the value $0{\cdot}7$ exactly, in other words, that it is a very simple fraction, while δN is converging to zero. This would be in accordance with views expressed by Halm.*

There is a strong case for further investigation, and we therefore employ a four-constant formula to fit the first four values of ρ_m. Thus we write

$$\rho_m = m+\mu+\alpha/(m+\mu)+\beta/(m+\mu)^2+\gamma/(m+\mu)^3 \tag{48}$$

and find that μ is then a solution of the cubic

$$\mu^3(\rho_4-3\rho_3+3\rho_2-\rho_1)+3\mu^2(4\rho_4-9\rho_3+6\rho_2-\rho_1) +3\mu(16\rho_4-27\rho_3+12\rho_2-\rho_1-8)+64\rho_4-81\rho_3+24\rho_2-\rho_1-60) = 0. \tag{49}$$

* 'Roy. Soc. Edin. Trans.,' vol. 41 (1906).

Neglecting terms in δN, this becomes

$$0{\cdot}004769\mu^3+0{\cdot}001284\mu^2-6{\cdot}007860\mu+4{\cdot}202764 = 0,$$

whence $$\mu = 0{\cdot}699922.$$

The convergence to the value 7/10 is still evident. If we include the terms in δN, the result is

$$\mu = 0{\cdot}699922+0{\cdot}0001598\,\delta N, \tag{50}$$

At the same time, γ is found to be so small that it is of no importance beyond $m = 1$. The application of the four-constant formula to the lines $m = 2$, 3, 4, and 5 would therefore lead to the value in (46),

or $$\mu = 0{\cdot}700149+0{\cdot}00003898\,\delta N.$$

The value of δN for a four-constant formula is therefore obtained by identifying the last two values. It becomes

$$\delta N = +1{\cdot}87, \tag{51}$$

or almost precisely zero again. There can be no doubt now that the value given by Curtis is absolutely correct for helium as well as hydrogen, and that the Rydberg form is the proper development for ρ_m—proper, of course, only in the sense of being most natural. For the more lines we use, the more definitely does δN converge to zero. The mean of the last two values is $-0{\cdot}25$, which is quite negligible.

The mean value of μ is now, from the last two values,

$$0{\cdot}700035+0{\cdot}0001208\,\delta N, \qquad \text{or } 0{\cdot}700005,$$

and that its value is exactly $0{\cdot}7$ cannot be doubted.

If we now, using the greatest possible accuracy, adopt $\mu = 0{\cdot}7$, $\delta N = 0$,

$$\rho_m = m+\mu+\alpha/(m+\mu)+\beta/(m+\mu)^2+\gamma/(m+\mu)^3, \tag{52}$$

we find, after some reduction,

$$\alpha = 0{\cdot}018546, \qquad \beta = -0{\cdot}077181, \qquad \gamma = 0{\cdot}02276,$$

the coefficients being alternately positive and negative. As anticipated, β is more important than α, and afterwards the convergence is rapid except for the first line.

The Sharp series becomes

$$\nu = 29223{\cdot}780-109679{\cdot}2/\rho_m{}^2,$$

where $$\rho_m = m+0{\cdot}7+\frac{0{\cdot}018546}{m+0{\cdot}7}-\frac{0{\cdot}077181}{(m+0{\cdot}7)^3}+\frac{0{\cdot}02276}{(m+0{\cdot}7)^3}. \tag{53}$$

The last term is practically negligible even for the line $m = 3$, and the last but one very soon afterwards. But the determination of these coefficients as precisely as possible will ultimately shed light on the nature of spectra.

The formula is not empirical in the ordinary sense, but has been shown to be of the necessary practical form. It is now evident that the values of ρ_m are not simple, and that no formula yet proposed is anything but an empirical approximation.

One remark may be made. It seems probable that the only way to regard the sequence $\rho_1, \rho_2, \ldots \rho_m$, is as the roots of a transcendental equation, and the probable nature of this equation can be suspected. For the equation

$$\tan x = a + b/x + c/x^2 + \ldots \tag{54}$$

has roots which express themselves naturally in this manner. The general behaviour of the coefficients is exactly in accordance with this view.

At the same time, if the Rydberg-Schuster law is true, Rydberg's constant is the same in hydrogen and helium, and *vice versâ*. The law is at the same time certainly true from the earlier part of this paper.

The Diffuse Series Constants.

In the Diffuse series, the investigation cannot be pushed so far, for the line $m = 1$ is far in the infra-red and unknown. But Eversheim has measured $m = 2$ (the line D_3) and $m = 3$ accurately enough for our purpose, and $m = 4$ is in the part of the spectrum, near $\lambda\,4000$, where accurate measurements are possible. But $m = 5$ in this series is known, from the work of Hicks, to be a bad measurement. Our conclusions must, therefore, be drawn from three accurate lines only. Nevertheless they are quite definite, as will appear. The limit of the series is given very accurately by

$$\lambda = 29223{\cdot}776 + 0{\cdot}004416\,\delta\mathrm{N},$$

and the wave numbers are

$$\nu_2 = 17014{\cdot}789, \qquad \nu_3 = 22357{\cdot}740, \qquad \nu_4 = 24830{\cdot}479,$$

so that the values of $\rho_m = (109679{\cdot}22 + \delta\mathrm{N})^{\frac{1}{2}}/(\mathrm{A} - \nu_m)^{\frac{1}{2}}$ are, on calculation,

$$\left.\begin{aligned} \rho_2 &= 2{\cdot}997245 + 0{\cdot}0^4 1312\,\delta\mathrm{N}, \\ \rho_3 &= 3{\cdot}996769 + 0{\cdot}0^4 1696\,\delta\mathrm{N}, \\ \rho_4 &= 4{\cdot}996510 + 0{\cdot}0^4 2027\,\delta\mathrm{N}. \end{aligned}\right\} \tag{55}$$

Since μ is nearly unity in this series, whatever formula be adopted, a Hicks formula, or, in fact, various forms, can give good results. If, for example, we use the Hicks form

$$\rho_m = m + \mu + \alpha/m,$$

then $\quad 4 + 2\mu + \alpha = 2\rho_1, \qquad 9 + 3\mu + \alpha = 3\rho_3, \qquad 16 + 4\mu + \alpha = 4\rho_4,$

whence $2\rho_2 + 4\rho_4 - 6\rho_3 = 2$, and, solving for $\delta\mathrm{N}$, we obtain

$$\delta\mathrm{N} = 15{\cdot}1. \tag{56}$$

This is already nearer to zero than to Bohr's value.

Now we have every reason to believe that the variable parts of the Diffuse and Sharp series are of the same type. Spectroscopists would hesitate to give up this opinion. If, therefore, we use the Sharp series type with only one constant α, we write

$$\rho_m = m+\mu+\alpha/(m+\mu),$$

and obtain two equations for μ and δN,

$$\mu = \frac{4\rho_4-3\rho_3-7}{2+\rho_3-\rho_4} = \frac{3\rho_3-2\rho_2-5}{2+\rho_2-\rho_3}.$$

The results of the arithmetical work are

$$\delta N = -26{\cdot}4, \qquad \mu = 0{\cdot}99635.$$

The value of δN has passed beyond zero, and when the type of formula found necessary for the Sharp series is employed, the choice lies between zero and a negative value. We cannot add another constant and proceed further, for we lack the line $m = 1$, the line $m = 5$ is inaccurate, and $m = 6$ is too far down to be of use with the present accuracy.

But we can proceed in another way. For in the case of the Sharp series the constant β is as important as α. This may be the case here. If so, a close value of δN can be found by (1) neglecting β as above, and (2) neglecting α, and (3) taking the mean of the two results. For the errors they produce in δN can be shown to be in opposite directions. If, therefore, neglecting α, we write

$$\rho_m = m+\mu+\beta/(m+\mu)^2,$$

and solve the resulting equations, we find, after some reduction,

$$\delta N = +25{\cdot}2.$$

The mean of the two values is $\delta N = \frac{1}{2}(25{\cdot}2-26{\cdot}4) = -0{\cdot}6$, and the true value is evidently again zero. At the same time, $\mu = 0{\cdot}996704$.

Another calculation has been made, by taking a corrected value for the line $m = 5$ from Hicks' investigation, and using both α and β. The value found for δN was about 3.

The best available value of μ is found by fitting a formula with three constants μ, α, β, to ρ_2, ρ_3, ρ_4, with $\delta N = 0$. The result is

$$\mu = 0{\cdot}994180,$$

but the calculation with $m = 5$ suggests that it is converging to $0{\cdot}994$. It is quite certain that μ is not equal to unity in the Diffuse series.

The more refrangible components of the Diffuse series are given by

$$\nu = 29223{\cdot}776-109679{\cdot}22/\rho_m^2,$$

where $$\rho_m = m+0{\cdot}99418+\frac{0{\cdot}023438}{m+0{\cdot}99418}-\frac{0{\cdot}074456}{(m+0{\cdot}99418)^2}.$$

The Principal Series.

It is perhaps unnecessary to give the complete investigation for the Principal series, which proceeds in the same manner. We again find, though with less accuracy on account of bad measurements, that δN converges closely to zero as the number of constants in the formula increases, and that the only satisfactory form is

$$\rho_m = m+\mu+\alpha/(m+\mu)+\beta/(m+\mu)^2+\ldots,$$

which is not very convergent for the first lines.

The leading line is known very accurately, and the next three are fairly reliable, from the results of previous series representations made by Hicks and others. The values of ρ are numerically

$$\rho_1 = 1{\cdot}937286, \qquad \rho_2 = 2{\cdot}933420,$$
$$\rho_3 = 3{\cdot}932255, \qquad \rho_4 = 4{\cdot}931434.$$

The limit is $A = 38454{\cdot}943$, and the value of μ calculated from the first four lines is $\mu = 0{\cdot}924507$. There is evidence, moreover, of a convergence to 0·925, which further measurements may confirm. Pending such measurements, the only interest of this investigation of the Principal series lies in the fact that N has again Curtis' value.

A consideration of the spectrum of parhelium is left for a later paper.

Summary.

1. The limits of series with many lines, for which a Hicks formula is already known, can be calculated with extreme accuracy by a new method.

2. The interferometer measures of the leading lines of the helium series enable the best form of the series to be obtained, and this form is an extension of that of Rydberg, dependent on $m+\mu$ and not m.

3. The value of Rydberg's constant 109679·2 given by Curtis for hydrogen is the true value for the arc spectrum of helium, and is in fact a rigorous constant for arc spectra. Spark spectra are not treated.

4. The Rydberg-Schuster law of limits is exact for helium.

5. It seems probable that μ is a simple fraction whose denominator is a multiple of 5, as Halm has suggested. It is exactly 0·7 for the Sharp series of helium.